Double Silylation of 1,4-Bis(trimethylsilyl)butadiyne with Disilanes Using a Palladium Catalyst

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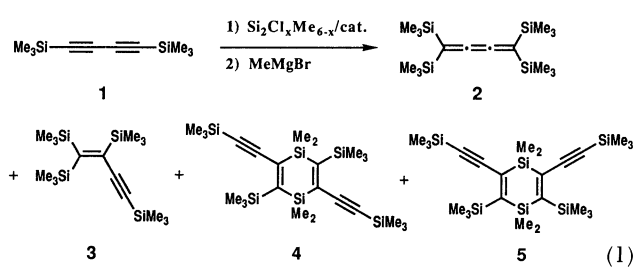
Reaction of 1,4-bis(trimethylsilyl)butadiyne with polychlorodisilanes $Si_2Cl_xMe_{6-x}$ in the presence of a palladium catalyst gives, after methylation, 1,1,4,4-tetrakis(trimethylsilyl)butatriene and/or 1,1,2,4-tetrakis-(trimethylsilyl)-1-buten-3-yne selectively. Hydrogenation, hydrosilylation, and oxidation of the obtained butatriene were found to take place at C(1)=C(2) double bond exclusively. The regioselectivity is ascribed to the geminally substituted silyl groups which sterically direct the attack of electrophile and stabilize postulated radical intermediates.

Double silylation of unsaturated compounds by means of disilanes is a useful synthetic method for disilyl organic compounds which are versatile synthetic building blocks and possible monomers for silicon-containing polymers. This type of reaction was first reported by Kumada et al. in 1972 who employed nickel catalysts.[1] Since then double silylation of acetylenes with tetramethyldisilane,[2] cyclic disilanes,[3] difluorotetramethyldisilane,[4] or chlorinated disilanes including "disilane fraction"[5] has been achieved using palladium catalysts. Conjugate dienes[6,7] and allenes[8] also undergo the double silylation. The reaction is carried out sometimes using a platinum catalyst[9] or a nonmetallic catalyst tetrabutylammonium fluoride.[10] However, no report has appeared on the double silylation of conjugate diynes. We report herein that 1, 4-bis(trimethylsilyl)butadiyne (**1**), a stable butadiyne substitute,[11-13] reacts with methylated chlorodisilanes in the presence of a palladium catalyst to afford 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**2**) and/or 1,1,2,4-tetrakis(trimethylsilyl)-1-buten-3-yne (**3**) depending on the structure of the catalyst and the disilane used.[14] We also studied the reactivity of the obtained butatriene **2** towards hydrogenation, hydrosilylation, and oxidation; all the reactions took place at C(1)=C(2) double bond.[15]

Double Silylation of 1,4-Bis(trimethylsilyl)butadiyne (1). Reaction of **1** with excess amount of "disilane fraction" (bp 145—155 °C, a 1:1 mixture of $MeCl_2Si$–$SiClMe_2$ and $MeCl_2Si$–$SiCl_2Me$) in the presence of a catalytic amount of $PdCl_2(PEt_3)_2$ followed by treatment with methylmagnesium bromide gave double silylation products **2** (42% yield) and **3** (18% yield)



(1)

along with $(SiMe_2)_n$[16] and small amounts of by-products tentatively assigned as **4** and **5** which were assumed to be derived from silylenes (Table 1, Run 5). When a series of $PdCl_2(PR_3)_2$ was employed, both reactivity and selectivity changed according to the structure of the phosphine ligand as shown in Table 1. In general, **2** was produced as the major product. Use of $PdCl_2(PMePh_2)_2$ or $PdCl_2(PMe_2Ph)_2$ resulted in the improvement of the yields of **2** and **3** (Runs 1—3). Palladium catalysts having a less bulky phosphine ligand were in general more active, but $PdCl_2(PMe_3)_2$ gave low yields of the products accompanied by many by-products (Run 4). The propensity was readily recognized in the examples of $PdCl_2[P(cyclohexyl)_3]_2$ (Run 9), $PdCl_2(PBu_3)_2$ (Run 8), $PdCl_2(PEt_3)_2$ (Run 5), and $PdCl_2(PMe_3)_2$ (Run 4). Although $PdCl_2[P(CH_2Ph)_3]_2$ (Run 7) and $Pd(PPh_3)_4$ (Run 10) were active enough, followings were totally inactive: $PdCl_2(PhCN)_2$, $PdCl_2[P(CH_2CH_2CN)_3]_2$, $PdCl_2(PHPh_2)_2$, $PdCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$, $PdCl_2[P(OMe)_3]_2$, $PdCl_2[P(NMe_2)_3]_2$, and $Pt(PPh_3)_4$. A nickel catalyst $NiCl_2(PPh_3)_2$ or $NiCl_2(PEt_3)_2$ gave complex mixtures.

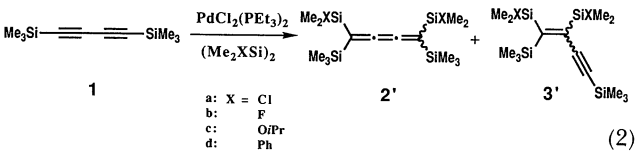
We next compared the reactivity of various disilanes. Both $MeCl_2Si$–$SiCl_2Me$ and $MeCl_2Si$–$SiClMe_2$ exhibited similar reactivity as "disilane fraction" and gave **2** and **3** in comparable yields in the presence of $PdCl_2(PEt_3)_2$ (Runs 5, 11, and 14) or $Pd(PPh_3)_4$ (Runs 10, 13, and 16). The $PdCl_2[P(CH_2Ph)_3]_2$ catalyst combined with $MeCl_2Si$–$SiCl_2Me$ gave the two products in higher yields (Run 12), but the same catalyst using $MeCl_2Si$–$SiClMe_2$ did less efficiently (Runs 7 and 15). The results indicate that $MeCl_2Si$–$SiCl_2Me$ of "disilane fraction" mainly reacted with the butadiyne **1**. The enyne **3** was obtained as the major product from Me_2ClSi–$SiClMe_2$ or Me_2ClSi–$SiMe_3$ in the presence of $PdCl_2(PEt_3)_2$ or $PdCl_2[P(CH_2Ph)_3]_2$ (Runs 17—20, 22, and 23). Hexamethyldisilane was the least reactive to give only a small amount of **3** (Runs 24—26). In contrast, hexachlorodisilane underwent polysilane formation solely. These results show that highly chlorinated disilanes prefer 1,4-disilylation to give **2**, whereas less chlorinated disilanes afford **3** by 1, 2-addition.

Table 1. Reaction of **1** with Disilanes[a]

Run	Disilane	Catalyst (mol%)		Conditions	Yield/%[b] 2	3
1	Disilane fraction[c]	$PdCl_2(PPh_3)_2$	(5.2)	120 °C, 10 h	19	8
2	Disilane fraction[c]	$PdCl_2(PMePh_2)_2$	(5.1)	120 °C, 9 h	36	23
3	Disilane fraction[c]	$PdCl_2(PMe_2Ph)_2$	(2.9)	120 °C, 7.5 h	20	24
4	Disilane fraction[c]	$PdCl_2(PMe_3)_2$	(2.9)	120 °C, 9 h	7	6
5	Disilane fraction[c]	$PdCl_2(PEt_3)_2$	(3.2)	100 °C, 10 h	42	18
6[d]	Disilane fraction[c]	$PdCl_2(PEt_3)_2$	(1.7)	120 °C, 9 h	49	23
7	Disilane fraction[c]	$PdCl_2[P(CH_2Ph)_3]_2$	(1.8)	110 °C, 5 h	29	29
8	Disilane fraction[c]	$PdCl_2(PBu_3)_2$	(2.9)	110 °C, 8 h	10	8
9[e]	Disilane fraction[c]	$PdCl_2[P(C_6H_{11}\text{-}c)_3]_2$	(2.1)	120 °C, 17 h	—	—
10	Disilane fraction[c]	$Pd(PPh_3)_4$	(4.1)	140 °C, 13 h	24	5
11	$MeCl_2SiSiCl_2Me$	$PdCl_2(PEt_3)_2$	(2.9)	100 °C, 5 h and 110 °C, 2 h	49	22
12	$MeCl_2SiSiCl_2Me$	$PdCl_2[P(CH_2Ph)_3]_2$	(3.1)	120 °C, 1 h	45	36
13	$MeCl_2SiSiCl_2Me$	$Pd(PPh_3)_4$	(3.2)	120 °C, 6 h	35	13
14	$MeCl_2SiSiClMe_2$	$PdCl_2(PEt_3)_2$	(3.8)	120 °C, 3 h	48	14
15	$MeCl_2SiSiClMe_2$	$PdCl_2[P(CH_2Ph)_3]_2$	(2.1)	120 °C, 5 h	12	11
16	$MeCl_2SiSiClMe_2$	$Pd(PPh_3)_4$	(3.3)	120 °C, 6 h	23	8
17	$Me_2ClSiSiClMe_2$	$PdCl_2(PEt_3)_2$	(1.6)	120 °C, 4 h	5	72
18	$Me_2ClSiSiClMe_2$	$PdCl_2[P(CH_2Ph)_3]_2$	(2.1)	120 °C, 10 h	Trace	52
19[f]	$Me_2ClSiSiClMe_2$	$PdCl_2[P(CH_2Ph)_3]_2$	(1.6)	120 °C, 11 h	4	74
20	$Me_2ClSiSiClMe_2$	$PdCl_2(PMe_3)_2$	(4.3)	120 °C, 16 h	3	36
21	$Me_2ClSiSiClMe_2$	$Pd(PPh_3)_4$	(3.8)	140 °C, 29 h and 160 °C, 22 h	6	7
22	$Me_2ClSiSiMe_3$	$PdCl_2(PEt_3)_2$	(4.4)	120 °C, 8 h	Trace	26
23	$Me_2ClSiSiMe_3$	$PdCl_2[P(CH_2Ph)_3]_2$	(2.1)	120 °C, 8 h	13	40
24[e]	$Me_3SiSiMe_3$	$PdCl_2(PEt_3)_2$	(5.1)	140 °C, 16 h	—	14
25[e]	$Me_3SiSiMe_3$	$PdCl_2[P(CH_2Ph)_3]_2$	(2.5)	140 °C, 17 h and 160 °C, 5 h	—	7
26[e]	$Me_3SiSiMe_3$	$PdCl_2(PMe_3)_2$	(4.1)	140 °C, 20 h	—	3

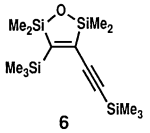
a) Typically a mixture of **1** (about 0.2 mmol), an excess (3—6 mol equiv) of a disilane, and a catalyst was heated under an argon atmosphere at the specified temperature for the noted period before quenching with excess MeMgBr. b) Isolated yields after purification by preparative TLC or column chromatography. c) A 1:1 mixture of $MeCl_2SiSiCl_2Me$ and $MeCl_2SiSiClMe_2$. d) Reaction of **1** (1.6 g, 8.2 mmol) with disilane fraction (3 g). e) Most of the starting material **1** was recovered. f) Reaction of **1** (1.5 g, 7.7 mmol) with $Me_2ClSiSiClMe_2$ (3 g).

Isolation of the primary silylation product without methylation allowed us to establish the stereochemical course of the disilylation. The reaction mixture of **1** with Me_2ClSi–$SiClMe_2$ using $PdCl_2(PEt_3)_2$ was subjected to GLC separation. Hereby only **3'a** was isolated which was proved to be a 1:1 *E*/*Z* mixture.



(2)

Other disilanes in Table 2 also exhibited similar nonselectivity. Three possible pathways for the formation of the *E*/*Z* isomers emerges: (1) stereochemically random disilylation, (2) cis-double silylation followed by *E*–*Z* isomerization under the reaction conditions as observed by Nagai et al.,[5] or (3) cis-double silylation and thermal isomerization upon GLC separation. To get an insight into the stereochemistry of the double silylation, we hydrolyzed the reaction mixture obtained from **1** and $(Me_2ClSi)_2$ and isolated a cyclic siloxane **6** (55% yield). Treatment of the primary disilylated product with



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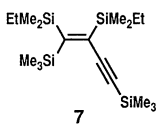

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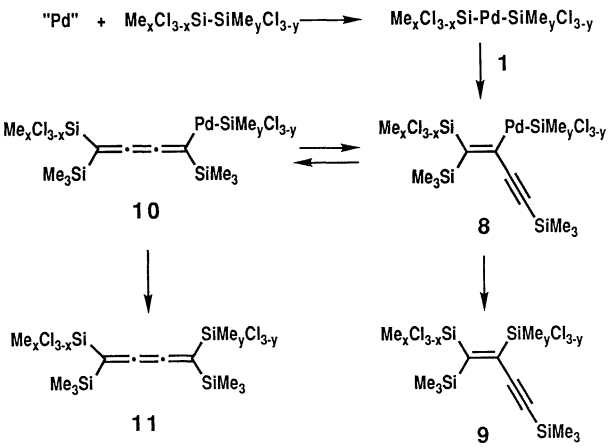
excess ethylmagnesium bromide afforded **7** in 64% overall yield as a single product after purification by preparative TLC. However, **7** isomerized into a 1:1 mixture of *E* and *Z* isomers upon GLC analysis at 200 °C. These experimental results suggest that the disilylation under the reaction conditions took place in a cis-manner, and the primary products are stereochemically stable under the reaction conditions (120 °C) or below 200 °C. Above 200 °C the *E*–*Z* isomerization takes place easily. The facile geometrical isomerization is characteristic of highly silylated ethenes.[17]

The double silylation reaction is considered to proceed through a mechanism shown in Scheme 1. Oxidative addition of low valent palladium species "Pd" is well-established to take place at the Si–Si bond of a disilane $Me_xCl_{3-x}Si$–$SiMe_yCl_{3-y}$ to give rise to an active species $Me_xCl_{3-x}Si$–Pd–$SiMe_yCl_{3-y}$. This adds across the triple bond of **1** through 1,2-*cis*-silylmetallation to give an alkenylpalladium **8** which was further

Table 2. Double Silylation of **1** Using $PdCl_2(PEt_3)_2$ Catalyst

Run	R_3SiSiR_3	Conditions	Product yield/%[a]
1	$Me_2ClSiSiClMe_2$	120 °C, 8 h	**3'a**[b] 61
2	$Me_2FSiSiFMe_2$	120 °C, 9 h	**3'b**[b] 86
3	$Me_2(i\text{-PrO})SiSi(OPr\text{-}i)Me_2$	120 °C, 9 h	**3'c**[b] 55
4	$Me_2PhSiSiPhMe_2$	120 °C, 6 h	**2'd**[b] 13 and **3'd**[b] 26

a) Isolated yields by GLC (Diasolid ZS, 6 mmϕ×3 m, 200 °C). b) A ca. 1:1 mixture of the *E* and *Z* isomers.

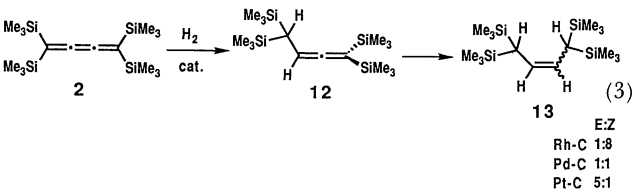


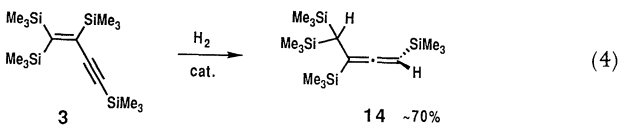
Scheme 1.

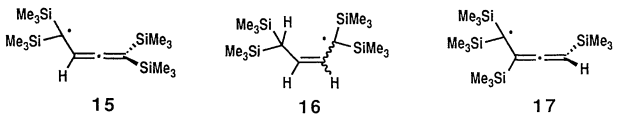
converted into **9** by reductive elimination. When a more chlorinated disilane was employed, the silicon ligand in **8** grew less nucleophilic to retard the final reductive elimination leading to **9**. Thus, the intermediate **10** would have been formed by 1,3-rearrangement of **8** before reductive elimination to give rise to **11**.

Reaction of the Butatriene 2 and the Butenyne 3. Butatrienes have two sp-hybridized central carbon atoms and two terminal sp^2-carbon atoms, and their reactivity is expected to be totally different from allenes or conjugated dienes. Although 1,2,3-butatrienes of general structure $R_2C{=}C{=}C{=}CR_2$ were accessible by various methods, studies on their reactions[18–24] were scarce. The triene **2** has been obtained by the reaction of bis(trimethylsilyl)acetylene with dicarbonyl(η^5-cyclopentadieny)cobalt,[25] photolysis of tetrakis(trimethylsilyl)cyclopentadienone,[26] or pyrolysis of hexakis(trimethylsilyl)-2-butyne.[27] The radical anion of **2** was generated from **1** and derived to hexakis(trimethylsilyl)-2-butyne.[28] In spite of the existing synthetic methods, the reactivity of **2** remained unexplored.[26] Since the butatriene **2** is now readily available by the reaction of **1** with $Si_2Cl_xMe_{6-x}$ in the presence of a palladium catalyst as discussed above, we studied the reactivity of the cumulate bonds of **2** and the conjugate system of **3** towards various reactants.

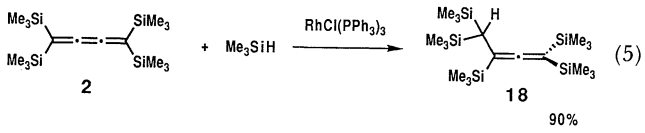
At first we studied hydrogenation of **2** and **3**. The hydrogenation of **2** with Rh-C, Pd-C, or Pt-C catalyst proceeded stepwise to give an allene **12** (IR 1910 cm^{-1}) first, which was further reduced to a tetrasilyl 2-butene **13**[29] under an atmospheric pressure of hydrogen at room temperature. A regioisomer of **12**, $(Me_3Si)_2C{=}CH{-}CH{=}C(SiMe_3)_2$, was not produced at all. On the contrary, hydrogenation of *cis*-1,4-diphenylbutatriene occurs at the central C=C bond to give 1,4-diphenyl-1,3-butadiene.[18] Thus, the C(2)=C(3) double bond of **2** resisted the addition of molecular hydrogen. Molecular model study of **2** clearly indicates that the π-electron cloud of the C(2)=C(3) double bond is heavily shielded by the four bulky trimethylsilyl groups at C(1) and C(4). Accordingly the coordination of the catalyst to this bond should be sterically disfavored. In contrast, an intermediary radical **15**, generated by the addition of a hydrogen radical across C(1)=C(2) of **2**, should be well-stabilized by the two silyl groups substituted on the radical center.[30] Thus, the formation of **12** is reasonably understood by assuming a radical intermediate **15**. Hydrogenation of the allene **12** with Rh-C catalyst proceeded from less crowded side to give (*Z*)-**13** mainly. On the other hand, reduction with Pt-C perhaps proceeded through a radical intermediate **16** to give rise to a thermodynamic product (*E*)-**13**. Hydrogenation of **3** with Pd-C afforded an allene **14** as a 1,4-reduction product which did not undergo further reduction. Herein a radical **17** might have been involved as a precursor of **14**. The fact that **14** resisted further reduction may be ascribed to the shielding of all π-orbitals by bulky silyl groups. Hydrogen radical transfer to **14**, if any, does not afford a radical stabilized by two silyl groups.





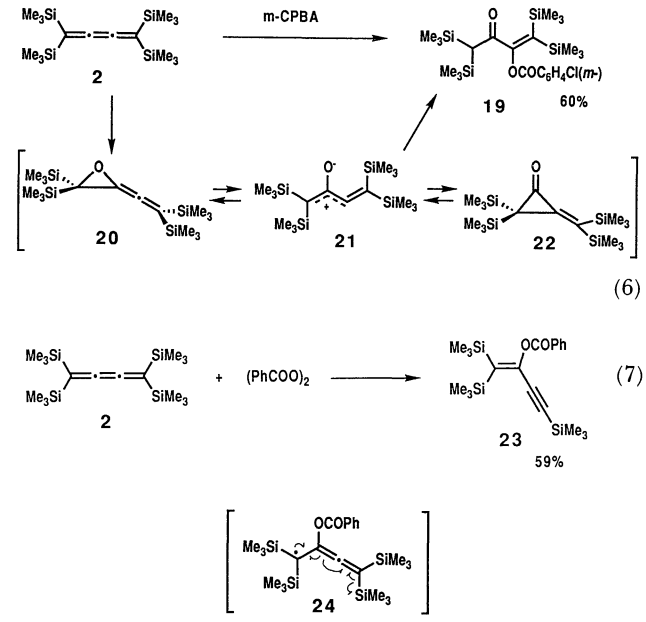


Hydrosilylation of **2** using trimethylsilane and a Rh catalyst proceeded at C(1)=C(2) to afford **18** in 90% yield. However, hydrosilanes like Et_3SiH, $PhMe_2SiH$, or Me_2ClSiH failed to react with **2**. These hydrosilanes whose steric bulk is apparently much larger suffered probably remarkable steric hindrance by the four trimethylsilyl groups. Hydrosilylation of **3** did not take place at all.



(5)

Oxidation of **2** was carried out with *m*-chloroperbenzoic acid (*m*-CPBA) at room temperature to give **19** in 60% yield. Formation of **19** is attributed to a facile isomerization of the initially produced epoxide **20** to an oxyallyl **21** followed by nucleophilic attack by the co-produced *m*-chlorobenzoic acid (*m*-CBA). The oxidation of 1,1,4,4-tetraphenylbutatriene[20] or tetraalkylbutatrienes[21] with *m*-CPBA is reported to give the corresponding cyclopropanones. The reactivity difference of **2** and 1,1,4,4-tetraalkylbutatrienes[21] may be understood in terms of the β-cation stabilizing effect of the trimethylsilyl groups in the oxyallyl **21**, which is captured by *m*-CBA before farther isomerization to a cyclopropanone **22**.[21,31]



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(7)

Benzoyl peroxide reacted with **2** to give **23** in 59% yield. The reaction is reasonably ascribed to an initial addition of benzoyloxy radical to C(2) to give a radical **24** followed by elimination of a trimethylsilyl radical. The regioselective addition of the benzoyloxyl radical observed in this reaction seems again to be governed by the silyl groups which stabilize a radical center and control the direction of the attack of PhCOO·.

We have demonstrated that disilylation of 1,4-bis(trimethylsilyl)butadiyne (**1**) gives tetrasilyl-substituted butatriene **2** and butenyne **3**. These as well as their hydrogenation products **13** and **14**, the hydrosilylation product **18**, and the oxidation products **19** and **24** are highly unsaturated C_4 compounds containing 3 to 5 trialkylsilyl groups. In view that alkyl- and vinylsilanes are versatile synthetic building blocks, the compounds prepared herein should find wide applications in organic synthesis.

Experimental

Melting points and boiling points are given in °C and are uncorrected. Bulb-to-bulb distillation was carried out using a Shibata glass tube oven GTO 250R, and boiling points were determined by measurement of the bath temperature and given in °C/Torr (1 Torr=133.322 Pa). ^1H NMR spectra were obtained with a Varian EM-390, a Hitachi R-90, or a Bruker AM-400 spectrometer, chemical shifts being given in ppm units, ^{13}C NMR spectra with a Varian XL-100 or a Bruker AM-400 spectrometer. Coupling constant J shown in ^{13}C NMR spectra means $J_{^{13}C-H}$. IR spectra were recorded with a JASCO A-202 machine. MS were recorded with a RMU-6MG spectrometer under 70 eV. High-resolution mass spectra were recorded with a Hitachi M-80A spectrometer. GLC assays were performed with a Shimadzu GC-7A chromatograph equipped with TCD or a Hitachi 163 gas chromatograph using FID, preparative GLC with an Ohkura Model-802T chromatograph equipped with TCD. TLC analyses were performed using Merck Silica gel 60 F_{254} glass plates (0.25 mm). Preparative TLC (1.2 mm thick) were prepared from Merck Kiesel-gel PF_{254}. The TLC mobility of a given component is expressed by its R_f value. Column chromatography was carried out with silica gel (Wakogel C-200) at atmospheric pressure.

Metal-Catalyzed Double Silylation of 1,4-Bis(trimethylsilyl)butadiyne (1) with Disilanes. A mixture of bis(trimethylsilyl)butadiyne (**1**) (35 mg, 0.18 mmol), "disilane fraction" (a 1:1 mixture of $MeCl_2Si$–$SiCl_2Me$ and $MeCl_2Si$–$SiClMe_2$, 0.12 ml, 217 mg), and dichlorobis(triethylphosphine)palladium (2.4 mg, 5.8×10^{-3} mmol) was placed in a 10 ml-sealed tube and heated at 100 °C for 10 h under an argon atmosphere. The reaction mixture was diluted with 5 ml of THF, transferred into a two-necked flask, and treated with 3 M (1 M=1 mol dm^{-3}) methylmagnesium bromide in diethyl ether (2.5 ml, 7.5 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, hydrolyzed with saturated sodium hydroxide aqueous solution (10 ml), and filtered through a Celite pad. The Celite pad was washed with diethyl ether (20 ml). The combined ethereal layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by preparative TLC (hexane) gave 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**2**) 26 mg (42% yield), 1,1,2,4-tetrakis(trimethylsilyl)-1-buten-3-yne (**3**) 11 mg (18%), and trace amounts of 2,5-bis(trimethylsilyl)-3,6-bis(trimethylsilylethynyl)-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**4**) and 2,6-bis(trimethylsilyl)-3,5-bis(trimethylsilylethynyl)-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**5**).

1,1,4,4-Tetrakis(trimethylsilyl)butatriene (2). Pale yellow prisms; mp 102—103 °C (lit,[18] 103—104 °C); R_f 0.9 (hexane). ^{1}H NMR ($CDCl_3$) δ=0.18 (s); ^{13}C NMR ($CDCl_3$) δ=0.52 (septuple q, J=2 and 119 Hz, 12C, $SiCH_3$), 157.1 (m, 2C, C(1) and C(4)), 205.6 (s, 2C, C(2) and C(3)); IR (KBr) 2980, 2920, 1550, 1260, 900, 840, 765, 690, 640, 620, 465 cm^{-1}; MS m/z (rel intensity) 342 (M^++2, 9), 341 (M^++1, 17), 340 (M^+, 43), 237 (55) 179 (67), 155 (35), 73 (100). Found: m/z 340.1890. Calcd for $C_{16}H_{36}Si_4$: M, 340.1892.

1,1,2,4-Tetrakis(trimethylsilyl)-1-buten-3-yne (3). A colorless oil; bp 95 °C/0.2 Torr; R_f 0.85 (hexane). ^{1}H NMR ($CDCl_3$) δ=0.18 (s, 9H), 0.23 (s, 9H), 0.28 (s, 9H), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$) δ=−0.21 (septuple q, J=2 and 120 Hz, $SiCH_3$), 1.82 (septuple q, J=2 and 120 Hz, $SiCH_3$), 2.20 (septuple q, J=2 and 120 Hz, $SiCH_3$), 3.16 (septuple q, J=2 and 120 Hz, $SiCH_3$), 107.1 (decuplet, J=2 Hz, C(4)), 110.4 (s, C(3)), 156.3 (m, C(1) or C(2)), 176.7 (m, C(1) or C(2)); IR (KBr) 2970, 2920, 2110, 1250, 910, 840, 760, 695, 640, 540 cm^{-1}; MS m/z (rel intensity) 342 (M^++2, 11), 341 (M^++1, 21), 340 (M^+, 53), 237 (80), 179 (76), 155 (55), 73 (100). Found: C, 56.26; H, 10.50%. Calcd for $C_{16}H_{36}Si_4$; C, 56.39; H, 10.65%.

2,5-Bis(trimethylsilyl)-3,6-bis(trimethylsilylethynyl)-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (4) and 2,6-Bis(trimethylsilyl)-3,5-bis(trimethylsilylethynyl)-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (5). A 2:1 mixture of **4** and **5** was isolated as colorless crystals; R_f 0.8 (hexane). IR (KBr) 2970, 2910, 2150 (w), 2120, 1480, 1410, 1245, 1075, 935, 840, 770, 700, 660, 570 cm^{-1}; MS m/z (rel intensity) 504 (M^+, 19), 155 (21), 73 (100).

Following absorptions are attributed to **4**: ^{1}H NMR ($CDCl_3$) δ=0.19 (s, 18H), 0.25 (s, 18H), 0.29 (s, 12H); ^{13}C NMR ($CDCl_3$) δ=−0.60 (qq, J=2 and 121 Hz, $Si(CH_3)_2$), −0.23 (septuple q, J=2 and 122 Hz, $Si(CH_3)_3$), 0.81 (septuple q, J=2 and 120 Hz, $Si(CH_3)_3$), 107.6 (decuplet, J=2 Hz, C≡CSiMe$_3$), 108.0 (s, C≡CSiMe$_3$), 155.5 (m, C(2) and C(5), or C(3) and C(6)), 171.1 (m, C(2) and C(5), or C(3) and C(6)).

Peaks of **5** are ^{1}H NMR ($CDCl_3$) δ=0.10 (s, 6H), 0.19 (s, 18H), 0.24 (s, 6H), 0.26 (s, 18H); ^{13}C NMR ($CDCl_3$) δ=−2.77 (qq, J=2 and 121 Hz, $Si(CH_3)_2$), −0.23 (mq, J=122 Hz, $Si(CH_3)_3$), 1.01 (mq, J=120 Hz, $Si(CH_3)_3$), 1.30 (qq, J=2 and 120 Hz, $Si(CH_3)_2$), 107.5 (s, C≡CSiMe$_3$), 107.9 (m, C≡CSiMe$_3$), 151.7 (m, C(2) and C(5), or C(3) and C(6)), 174.7 (m, C(2) and C(5), or C(3) and C(6)).

In a similar manner the butadiyne **1** was allowed to react with "disilane fraction", 1,2-dimethyl-1,1,2,2-tetrachlorodisilane, 1,1,2-trichloro-1,2,2-trimethyldisilane, 1,2-dichloro-1,1,2,2-tetramethyldisilane, chloropentamethyldisilane, or hexamethyldisilane using several palladium catalysts. The crude products were treated with methylmagnesium bromide, and the permethylated product **2**, **3**, **4**, or **5** was isolated respectively.

Synthesis of 2. In a two-necked flask fitted with a reflux condenser, were placed the butadiyne **1** (1.6 g, 8.2 mmol), dichlorobis(triethylphosphine)palladium (57 mg, 0.14 mmol), and "disilane fraction" (3 g), and the mixture was heated at 120 °C for 9 h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (10 ml) and then treated with 3 M methylmagnesium bromide in diethyl ether (20 ml, 60 mmol) at −40 °C. The reaction mixture was stirred for 2 h at 0 °C, quenched with saturated sodium hydroxide aqueous solution (30 ml), acidified with 2 M hydrochloric acid (5 ml), and extracted with diethyl ether (50 ml). The ethereal layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by recrystallization from methanol gave 1.2 g of **2** (42%). The filtrate, was concentrated, and the residue was subjected to column chromatography (hexane) to give additional **2** (190 mg, 7%) along with **3** (650 mg, 23%).

Synthesis of 3. In a two-necked flask fitted with a reflux condenser, were placed **1** (1.5 g, 7.7 mmol), dichlorobis(tribenzylphosphine)palladium (100 mg, 0.13 mmol), and 1,2-dichloro-1,1,2,2-tetramethyldisilane (3g, 16 mmol), and the mixture was heated at 120 °C for 11 h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (10 ml), treated with 3 M methylmagnesium bromide in diethyl ether (15 ml, 45 mmol) at −40 °C, and stirred for 2 h at 0 °C before quenching with saturated sodium hydroxide aqueous solution (30 ml). Acidification with 2 M hydrochloric acid (5 ml), extraction with diethyl ether (50 ml), drying the ethereal layer over anhydrous sodium sulfate, and concentration under reduced pressure, followed by purification by column chromatography (hexane), gave **2** 111 mg (4%) and **3** 1.94 g (74%).

1,2-Bis(chlorodimethylsilyl)-1,4-bis(trimethylsilyl)-1-buten-3-yne (3'a). A mixture of the butadiyne **1** (88 mg, 0.45 mmol), 1,2-dichloro-1,1,2,2-tetramethyldisilane (300 mg, 1.6 mmol), and dichlorobis(triethylphosphine)palladium (2.8 mg, 6.8×10^{-3} mmol) was placed in a 10 ml-sealed tube and heated at 120 °C for 8 h under an argon atmosphere. Isolation by GLC (Diasolid ZS, 6 mm$\phi\times$3 m, injection temp. 220 °C, column temp 200 °C, retention time 10 min) gave **3'a** (105 mg, 61% yield) as a 1:1 mixture of E/Z isomers. A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.20 (s, 18H), 0.356 (s, 9H), 0.358 (s, 9H), 0.68 (s, 6H), 0.70 (s, 9H), 0.71 (s, 6H), 0.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.54 (mq, J=120 Hz, $Si(CH_3)_3$), −0.50 (mq, J=120 Hz, $Si(CH_3)_3$), 1.78 (mq, J=120 Hz, $Si(CH_3)_3$), 3.07 (mq, J=120 Hz, $Si(CH_3)_3$), 4.30 (qq, J=2 and 121 Hz, $SiCl(CH_3)_2$), 4.36 (qq, J=2 and 121 Hz, $SiCl(CH_3)_2$), 5.22 (qq, J=2 and 121 Hz, $SiCl(CH_3)_2$), 6.37 (qq, J=2 and 121 Hz, $SiCl(CH_3)_2$), 107.9 (s, C(3)), 108.0 (s, C(3)), 111.0 (decuplet, J=2 Hz, C(4)), 111.9 (decuplet, J=2 Hz, C(4)), 151.4 (m, C(1) or C(2)), 153.3 (m, C(1) or C(2)), 175.2 (m, C(1) or C(2)), 177.2 (m, C(1) or C(2)); IR (neat) 2960, 2120, 1410, 1250, 1040, 930, 835, 790, 690, 660 cm^{-1}; MS m/z (rel intensity) 384 (M^++4, 1), 383 (M^++3, 2), 382 (M^++2, 4), 381 (M^++1, 2), 380 (M^+, 5), 272 (17), 179 (22), 164 (32), 155 (17), 97 (12), 93 (18), 73 (100), 45 (20), 18 (20).

In a similar manner the butadiyne **1** was allowed to react with 1,2-difluoro-1,1,2,2-tetramethyldisilane, 1,2-bis(1-methylethoxy)-1,1,2,2-tetramethyldisilane, or 1,2-diphenyl-1,1,2,2-tetramethyldisilane using a dichlorobis(triethylphosphine)-palladium catalyst. The product **3'b**, **3'c**, **2'd**, or **3'd** respectively was isolated by GLC.

1,2-Bis(fluorodimethylsilyl)-1,4-bis(trimethylsilyl)-1-buten-3-yne (3'b). A 1:1 mixture of E/Z isomers was isolated as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.189 (s, 9H), 0.190 (s, 9H), 0.281 (s, 9H), 0.283 (s, 9H), 0.34 (d, J=2.6 Hz, 6H), 0.36 (d, J=2.5 Hz, 6H), 0.42 (d, J=1.7 Hz, 6H), 0.43 (d, J=1.7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.80 (qdq, J=1, 4, and 120 Hz, $SiF(CH_3)_2$), −0.65 (qdq, J=1, 4, and 120 Hz, $SiF(CH_3)_2$), −0.43 (septuple q, J=2 and 120 Hz, $(Si(CH_3)_3)\times2$), 1.02 (mq, J=120 Hz, $Si(CH_3)_3$), 1.11 (dqd, J=2, 5, and 120 Hz, $SiF(CH_3)_2$), 1.27 (dqd, J=2, 5, and 120 Hz, $SiF(CH_3)_2$, 107.7 (s, C(4)), 107.8 (s, C(4)), 110.32 (m, C(3)), 110.33 (m, C(3)), 152.4

(md, J=4 Hz, C(1) or C(2)), 152.6 (md, J=5 Hz, C(1) or C(2)), 174.2 (md, J=3 Hz, C(1) or C(2)), 174.3 (md, J=4 Hz, C(1) or C(2)); MS m/z (rel intensity) 348 (M^+, 9), 256 (37), 241 (62), 164 (79), 155 (30), 73 (100), 45 (18).

1,2-Bis[dimethyl(1-methylethoxy)silyl]-1,4-bis(trimethylsilyl)-1-buten-3-yne (3'c). A 1:1 mixture of E/Z isomers. A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.16 (s, 9H), 0.19 (s, 9H), 0.21 (s, 9H), 0.23 (s, 6H), 0.24 (s, 9H), 0.25 (s, 6H), 0.34 (s, 6H), 0.35 (s, 6H), 1.16 (d, J=5.1 Hz, 12H), 1.21 (d, J=6.1 Hz, 12H), 3.9—4.1 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−0.36 (mq, J=120 Hz, Si(CH_3)$_3$), −0.33 (mq, J=120 Hz, Si(CH_3)$_3$), 0.52 (qq, J=2 and 120 Hz, Si(CH_3)$_2$), 0.63 (qq, J=2 and 119 Hz, Si(CH_3)$_2$), 1.05 (qq, J=2 and 120 Hz, Si(CH_3)$_2$), 2.06 (qq, J=2 and 119 Hz, Si(CH_3)$_2$), 2.20 (septuple q, J=2 and 120 Hz, Si(CH_3)$_3$), 2.77 (septuple q, J=2 and 119 Hz, Si(CH_3)$_3$), 25.7 (qq, J=5 and 125 Hz, OCH(CH_3)$_2$), 25.9 (qq, J=5 and 125 Hz, OCH(CH_3)$_2$), 64.8 (md, J=140 Hz, OCH(CH$_3$)$_2$), 66.1 (md, J=140 Hz, OCH(CH$_3$)$_2$), 106.5 (decuplet, J=2 Hz, C(4)), 107.4 (decuplet, J=2 Hz, C(4)), 110.3 (s, C(3)), 110.8(s, C(3)), 151.6 (m, C(1) or C(2)), 153.2 (m, C(1) or C(2)), 177.1 (m, C(1) or C(2)), 180.3 (m, C(1) or C(2)); IR(neat) 2970, 2910, 2100, 1250, 1120, 1020, 840, 780, 640 cm^{-1}; MS m/z (rel intensity) 428 (M^+, 7), 327 (28), 311 (17) 253 (51), 229 (40), 149 (29), 147 (29), 117 (41), 75 (100), 73 (90).

1,4-Bis(dimethylphenylsilyl)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (2'd). A 1:1 mixture of E/Z isomers. A yellow oil; R_f 0.5 (Hexane). IR (neat) 2970, 1545, 1430, 1250, 1110, 895, 840, 800, 780, 730, 700, 650, 620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.01 (s, 18H), 0.07 (s, 18H), 0.36 (s, 12H), 0.47 (s, 12H), 7.25—7.4 (m, 12H), 7.47—7.56 (m, 8H); MS m/z (rel intensity) 464 (M^+, 12), 299 (10), 290 (10), 241 (9), 197 (11), 135(100), 73 (25).

1,2-Bis(dimethylphenylsilyl)-1,4-bis(trimethylsilyl)-1-buten-3-yne (3'd). Isolated as a 1:1 mixture of E/Z isomers. A colorless oil; R_f 0.5 (Hexane). IR (neat) 2970, 2150, 2100, 1540, 1430, 1250, 1115, 900, 840, 780, 730, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.66 (s, 9H), −0.05 (s, 9H), 0.10 (s, 6H), 0.13 (s, 9H), 0.16 (s, 9H), 0.47 (s, 6H), 0.51 (s, 6H), 0.55 (s, 6H), 7.25—7.40 (m, 12H), 7.47—7.56 (m, 8H); MS m/z (rel intensity) 464 (M^+, 6), 271 (12), 217 (10), 197 (12), 135(100), 73 (27).

3-Trimethylsilyl-4-(2-trimethylsilylethynyl)-2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopent-3-ene (6). A mixture of **1** (39 mg, 0.2 mmol), 1,2-dichloro-1,1,2,2-tetramethyldisilane (0.2 ml), and dichlorobis(triethylphosphine)palladium (2.0 mg, 4.8×10^{-3} mmol) was placed in a 10 ml-sealed tube and heated at 110 °C for 4 h under an argon atmosphere. The reaction mixture was freed in vacuo of excess of the disilane. The residue was dissolved in diethyl ether (1 ml) and quenched with 1 M sodium hydroxide aqueous solution (2 ml) at room temperature for 0.5 h. The reaction mixture was poured to 1 M sodium hydroxide aqueous solution (10 ml) and extracted with diethyl ether (20 ml). The ethereal layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by preparative TLC (hexane:ethyl acetate=20:1, R_f 0.4) gave 36 mg of **6** (55% yield) as colorless prisms, mp 41 °C. ^{1}H NMR ($CDCl_3$) δ=0.18 (s, 9H), 0.20 (s, 9H), 0.22 (s, 6H), 0.25 (s, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.64 (qq, J=1 and 120 Hz, Si(CH_3)$_2$), −0.36 (septuple q, J=2 and 119 Hz, Si(CH_3)$_3$), −0.05 (septuple q, J=2 and 120 Hz, Si(CH_3)$_3$), 1.50 (qq, J=2 and 120 Hz, Si(CH_3)$_2$), 105.7 (s, C≡CSiMe$_3$), 107.6 (decuplet, J=3 Hz, C≡CSiMe$_3$), 157.6 (m, C(3) or C(4)), 176.6 (m, C(3) or C(4)); MS m/z (rel intensity) 326 (M^+, 30), 311 (49), 223 (39), 73 (100). Found: m/z 326.1370. Calcd for $C_{14}H_{30}OSi_4$: M, 326.1372.

(Z)-1,2-Bis(dimethylethylsilyl)-1,4-bis(trimethylsilyl)-1-buten-3-yne (7). In a similar manner the butadiyne **1** (31.5 mg, 0.16 mmol) was allowed to react with 1,2-dichloro-1,1,2,2-tetramethyldisilane (125 mg, 0.67 mmol) using dichlorobis(triethylphosphine)palladium (1.1 mg, 2.7×10^{-3} mmol). The crude product was treated with ethylmagnesium bromide. After workup the product **7** (38.5 mg, 64% yield) was isolated by preparative TLC (hexane, R_f 0.9) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 9H), 0.18 (s, 6H), 0.23 (s, 6H), 0.26 (s, 9H), 0.68 (q, J=7.9 Hz, 3H), 0.96 (t, J=7.9 Hz, 3H); IR (neat) 2970, 2200, 1440, 1250, 1165, 1050, 960, 900, 840, 780, 690, 635, 600, 540 cm^{-1}; MS m/z (rel intensity) 369 (M^++1, 11). 368 (M^+, 29), 251 (18), 237 (27), 193 (24), 169 (16), 155 (22), 87 (54), 73 (100), 59 (86). Found: m/z 368.2211. Calcd for $C_{18}H_{40}Si_4$: M, 368.2205.

Isomerization of 7 by Preparative GLC. The E and Z mixture (18.5 mg) was obtained from (Z)-butenyne **7** (20 mg) by preparative GLC (Diasolid ZS, 6 mmϕ×3 m, injection temp 220 °C, column temp 200 °C, retention time 15 min). The mixture showed ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 18H, Si(CH_3)$_3$ of E and Z), 0.18 (s, 6H, Si(CH_3)$_2$Et of E), 0.20 (s, 9H, Si(CH_3)$_3$ of Z), 0.233 (s, 6H, Si(CH_3)$_2$Et of E), 0.235 (s, 6H, Si(CH_3)$_2$Et of Z), 0.24 (s, 6H, Si(CH_3)$_2$Et of Z), 0.27 (s, 9H, Si(CH_3)$_3$ of E), 0.6—0.8 (m, 12H, SiCH_2CH$_3$ of E and Z), 0.8—1.0 (m, 18H, SiCH$_2$CH_3 of E and Z).

(E)-1,1,4,4-Tetrakis(trimethylsilyl)-2-butene [(E)-13]. This compound was prepared according to the procedure described in ref. 29: bp 70 °C/4 Torr (Lit,[29] 135—140 °C/10 Torr); mp 68—69 °C; R_f 0.95 (hexane). ^{1}H NMR ($CDCl_3$) δ=0.04 (s, 36H), 1.00 (dd, J=3.2 and 7.5 Hz, 2H), 5.02 (dd, J=3.2 and 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=0.07 (mq, J=119 Hz), 25.2 (mtd, J=6 and 108 Hz), 125.5 (dtd, J=1, 7, and 149 Hz); IR (KBr) 2960, 1245, 1115, 1030, 830, 770, 750, 680 cm^{-1}.

Hydrogenation of 2. A mixture of **2** (33.2 mg, 9.7×10^{-2} mmol), 10% palladium on carbon (3.5 mg), and methanol (0.5 ml) was stirred for 12 h at room temperature under a hydrogen atmosphere. The reaction mixture was filtered using a sintered-glass filter to remove the catalyst. The residue was washed with diethyl ether. The combined ethereal solution was concentrated under reduced pressure, and the residue was purified by preparative TLC (hexane, R_f 0.95) to give **13** (28 mg) as a 1:1 mixture of E and Z isomers. The mixture showed ^{1}H NMR ($CDCl_3$) δ=0.02 (s, 36H, Z), 0.04 (s, 36H, E), 0.99 (dd, J=3.2 and 7.5 Hz, 2H, E), 1.27 (dd, J=2.6 and 8.7 Hz, 2H, Z), 5.00 (dd, J=3.2 and 7.5 Hz, 2H, E), 5.13 (dd, J=2.6 and 8.7 Hz, 2H, Z); IR (neat) 2970, 1250, 1120, 1040, 850, 770, 740, 690 cm^{-1}.

A mixture of **2** (20.2 mg, 6×10^{-2} mmol), 10% palladium on carbon (19.5 mg), and methanol (0.5 ml) was stirred for 1 h at room temperature under a hydrogen atmosphere. The reaction mixture was filtered through a sintered-glass filter and concentrated under reduced pressure. Purification by preparative TLC (hexane, R_f 0.95) gave **12** and **13** as a mixture (21.2 mg, **12**:(E)-**13**:(Z)-**13**=4:1:2). The mixture showed ^{1}H NMR ($CDCl_3$) δ=0.02 (s, Si(CH_3)$_3$ of (E)-**13**), 0.05 (s, Si(CH_3)$_3$ of (Z)-**13**), 0.06 (s, 18H, Si(CH$_3$)$_3$×2 of **12**), 0.12 (s, 18H, Si(CH_3)$_3$×2 of **12**), 0.68 (d, J=10.8 Hz, 1H, CHSi$_2$ of **12**),

0.98 (dd, J=3.2 and 7.5 Hz, (*E*)-**13**), 1.27 (dd, J=2.6 and 8.7 Hz, (*Z*)-**13**), 4.30 (d, J=10.8 Hz, 1H, C=C<u>H</u> of **12**), 5.00 (dd, J=3.2 and 7.5 Hz, (*E*)-**13**), 5.13 (dd, J=2.6 and 8.7 Hz, (*Z*)-**13**); IR (neat) 2980, 1910 (C=C=C), 1250, 1050, 1030, 890, 840, 760, 690 cm^{-1}.

Hydrogenation of 3. A mixture of **3** (33.2 mg, 9.7×10^{-2} mmol), 10% palladium on carbon (10.6 mg), and methanol (0.5 ml) was stirred for 1 h at room temperature under a hydrogen atmosphere. The reaction mixture was filtered through a sintered-glass filter and concentrated under reduced pressure. Purification by preparative TLC (hexane, R_f 0.95) gave a product (15 mg) which contained **14** as a main component. ^1H NMR ($CDCl_3$) δ=0.049 (s, 9H), 0.055 (s, 9H), 0.075 (s, 9H), 0.086 (s, 9H), 0.265 (s, 1H), 4.51 (s, 1H); IR (neat) 2980, 1900 (C=C=C), 1250, 1030, 840, 770, 690 cm^{-1}; MS m/z (rel intensity) 342 (M^+, 8), 239 (23), 181 (15), 168 (19), 73 (100).

Hydrosilylation of 2 with Trimethylsilane. In a sealed tube were placed 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**2**) (40 mg, 0.12 mmol), chlorotris(triphenylphosphine)rhodium(I) (2.0 mg, 2.2×10^{-3} mmol), and trimethylsilane (240 mg, 3.2 mmol) at −78 °C, and the mixture was heated at 80 °C for 12 h. The reaction mixture was filtered through a short silica-gel column (Wakogel C-100, 20 mm$\phi\times$20 mm). Elution with diethyl ether (30 ml), and concentration of the eluate under reduced pressure, followed by preparative TLC (hexane, R_f 0.9) of the residue gave 1,1,3,4,4-pentakis(trimethylsilyl)-1,2-butadiene (**18**) 44 mg (90% yield). Recrystallization from methanol gave the analytically pure sample of **18** as colorless prisms; mp 94—95 °C. ^1H NMR ($CDCl_3$) δ=0.06 (s, 9H), 0.11 (s, 18H), 0.15 (s, 18H), 0.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.15 (septuple q, J=2 and 119 Hz, C(3)–Si(<u>C</u>H_3)$_3$), 1.58 (septuple q, J=2 and 119 Hz, C(1)–Si(<u>C</u>H_3)$_3$), 1.83 (decuple q, J=2 and 119 Hz, C(4)–Si(<u>C</u>H_3)$_3$), 14.56 (md, J=109 Hz, <u>C</u>(4)), 73.82 (m, <u>C</u>(1) or <u>C</u>(3)), 78.76 (m, <u>C</u>(1) or <u>C</u>(3)), 205.5 (d, J=11 Hz, <u>C</u>(2)); IR (KBr) 2970, 1860 (C=C=C), 1250, 885, 840, 760, 690 cm^{-1}; MS m/z (rel intensity) 414 (M^+, 12), 341 (13), 253 (22), 228 (11), 155 (40), 73 (100). Found: C, 54.69; H, 11.32%. Calcd for $C_{19}H_{46}Si_5$: C, 54.99; H, 11.17%.

Reaction of 2 with *m*-CPBA. A mixture of **2** (0.34 g, 1 mmol), *m*-CPBA (0.7 g, 4 mmol), and dichloromethane (2 ml) was stirred at room temperature for 20 min under an argon atmosphere. The mixture was treated with 20% sodium hydrogensulfite aqueous solution (3 ml), and stirring was continued for 20 min. To this solution was added sat. sodium hydrogencarbonate aq solution (20 ml), and the resulting mixture was extracted with chloroform (20 ml×2). The extract was washed with water (20 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Purification by preparative TLC (hexane:ethyl acetate=9:1, R_f 0.5) afforded 1,1,4,4-tetrakis(trimethylsilyl)-3-(3-chlorobenzoyloxy)-3-buten-2-one (**19**) 0.3 g (60% yield) as colorless prisms; mp 103 °C (methanol). ^1H NMR ($CDCl_3$) δ=0.07 (s, 18H), 0.14 (s, 9H), 0.26 (s, 9H), 2.38 (s, 1H), 7.49 (t, J=7.9 Hz, 1H), 7.63 (ddd, J=1.1, 2.1 and 7.9 Hz, 1H), 8.00 (ddd, J=1.1, 1.5 and 7.9 Hz, 1H), 8.09 (dd, J=1.5 and 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.45 (mq, J=120 Hz, C(4)–Si(<u>C</u>H_3)$_3$), 2.34 (septuple q, J=2 and 120 Hz, C(1)–Si(<u>C</u>H_3)$_3$), 2.96 (septuple q, J=2 and 119 Hz, C(1)–Si(<u>C</u>H_3)$_3$), 35.8 (md, J=111 Hz, <u>C</u>(4)), 128.1 (dtd, J=1, 7, and 165 Hz, <u>C</u>(4) or <u>C</u>(6) of C_6H_4Cl), 130.1 (dtd, J=1, 6, and 168 Hz, <u>C</u>(4) or <u>C</u>(6) of C_6H_4Cl), 130.3 (d, J=165 Hz, <u>C</u>(5) of C_6H_4Cl), 131.6 (d, J=9 Hz, <u>C</u>(3) of C_6H_4Cl), 133.9 (ddd, J=5, 8, and 167 Hz, <u>C</u>(2) of C_6H_4Cl), 135.2 (dtd, J=1, 3, and 5 Hz, <u>C</u>(1) of C_6H_4Cl), 140.7 (m, <u>C</u>(1)), 154.6 (s, <u>C</u>(2)), 164.1 (dt, J=2 and 8 Hz, <u>C</u>OO), 195.59 (d, J=5 Hz, <u>C</u>(3)); IR (KBr) 2960, 1730, 1680, 1250, 1030, 855, 740 cm^{-1}; MS m/z (rel intensity) 499 (M^++2−Me, 1.3), 497 (M^+−Me, 2.3), 187 (28), 148 (12), 147 (74), 139 (29), 111 (11), 99 (16), 73 (100). Found: C, 53.60; H, 8.06; Cl, 6.82%. Calcd for $C_{23}H_{41}ClO_4Si_4$: C, 53.81; H, 8.05; Cl, 6.91%.

Reaction of 2 with Benzoyl Peroxide. In a flask fitted with a reflux condenser, were placed **2** (34 mg, 0.1 mmol) and benzoyl peroxide (85 mg, 0.35 mmol) dissolved in 1,1,1-trichloroethane (0.5 ml), and the mixture was refluxed for 0.5 h under an argon atmosphere. The reaction mixture was quenched by the addition of 20% sodium hydrogensulfite aqueous solution (2 ml), and the stirring was continued for 20 min. To this solution was added sat. sodium hydrogencarbonate aq solution (5 ml), and the resulting mixture was extracted with chloroform (10 ml×2). The combined extract was washed with water (10 ml), dried over anhyd sodium sulfate, and concentrated under reduced pressure. Purification by preparative TLC (hexane:ethyl acetate=9:1, R_f 0.4) gave 1,1,4-tris(trimethylsilyl)-2-benzoyloxy-1-buten-3-yne (**23**) 23 mg (59% yield). Recrystallization from methanol gave pure **23** as colorless prisms; mp 44 °C. ^1H NMR ($CDCl_3$) δ=0.12 (s, 9H), 0.18 (s, 9H), 0.32 (s, 9H), 7.35—7.68 (m, 3H), 7.95—8.22 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.58 (septuple q, J=2 and 120 Hz, C(4)–Si(<u>C</u>H_3)$_3$), 1.31 (septuple q, J=2 and 120 Hz, C(1)–Si(<u>C</u>H_3)$_3$), 1.66 (septuple q, J=2 and 120 Hz, C(1)–Si(<u>C</u>H_3)$_3$), 96.85 (decuplet, J=2 Hz, <u>C</u>(4)), 100.8 (s, <u>C</u>(3)), 128.5 (dd, J=8 and 162 Hz, Ph), 130.1 (t, J=8 Hz, Ph), 130.2 (ddd, J=5, 6, and 160 Hz, Ph), 133.3 (ddd, J=7, 8, and 161 Hz, Ph), 134.8 (m, <u>C</u>(1)), 140.9 (s, <u>C</u>(2)), 164.1 (t, J=4 Hz, <u>C</u>OO); IR (KBr) 2970, 2150, 1740, 1555, 1450, 1260, 1250, 1110, 1080, 1060, 1020, 900, 840, 760, 710 cm^{-1}; MS m/z (rel intensity) 388 (M^+, 1), 283 (5), 179 (38), 105 (100), 77 (16), 73 (34). Found; C, 61.51; H, 8.15%. Calcd for $C_{20}H_{32}O_2Si_3$; C, 61.80; H, 8.30%.

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